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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PIGMENTABLE BINDER COMPOSITION

(57) **Abstract:** The present invention provides a pigmentable binder composition for use in synthetic asphalt, which composition comprises a resin, a lubricating oil and/or a lubricating oil extract, and in the range of from 0.05 to less than 3 %wt based on total composition of an amide additive of general formula: $R^1\text{-CO-N}(\text{CH}_2)_x\text{-N-CO-R}^2$, wherein R^1 and R^2 each independently represent alkyl groups having in the range of from 10 to 60 carbon atoms, and x is an integer in the range of from 1 to 4 and a synthetic asphalt comprising a mixture of aggregate and said pigmentable binder composition.



WO 03/062315 A1

Pigmentable Binder Composition

The present invention relates to a pigmentable binder composition and a synthetic asphalt comprising a pigmentable binder composition.

Background of the Invention

5 Bitumen is a widely used civil engineering material. The principal use of bitumen is in the construction of road and pavement surfaces, wherein a bituminous binder is mixed with aggregate to form asphalt. Bitumen is also used in industrial applications e.g. as a roofing
10 material or a pipe coating.

Bituminous materials are generally black or brown in appearance; bitumen generally being a residual product obtainable from the refining of crude oil. The appearance of bituminous road or pavement surfaces is considered
15 acceptable for most applications. However, in some locations it is desirable to have a surface in a specific colour, for example to denote cycle paths, bus lanes, pedestrian zones, or play areas etc. Further, in certain applications such as tunnel road surfaces it is preferred
20 to have a very light coloured surface in order to improve visibility.

The colour of bituminous materials may be modified by adding a pigment such as iron oxide and/or by use of coloured aggregates. However, the only acceptable colour
25 that can be achieved in this way is red. Further, where a pigment is used a large quantity of pigment is often required to achieve the desired effect.

To overcome this problem pigmentable binder compositions based upon non-bituminous constituents such
30 as resins, lubricating oils, lubricating oil extracts and

polymers have been developed. Pigmentable binders are defined as non-bituminous binders that may be coloured by the addition of pigments or coloured aggregate. Whilst the chemical composition of pigmentable binders is very different to bitumen, pigmentable binders have rheological properties similar to those of bituminous binders but have the advantage that they may be pigmented into a wide range of colours. Examples of known pigmentable binders are described in GB 1226234, EP-A 0179510 and EP-A 0330281. Pigmentable binders are sometimes referred to as synthetic binders as they do not contain asphaltenes (asphaltenes being the constituent of bitumen giving it its black colouring) and asphalts prepared from pigmentable binders may be referred to as synthetic asphalts.

For certain applications such as indoor floorings it is advantageous to apply a surfacing as a mastic asphalt. Mastic asphalt is a particular type of binder/aggregate mixture that is hand-laid by workers who use wooden floats to work the material into shape at high temperature. When laying conventional mastic asphalt, it is necessary for the mixture of binder and aggregate to be heated to extremely high temperatures of up to 240 °C in order to ensure good workability. Such high application temperatures do not adversely affect the properties of bituminous binders. However, the constituents of pigmentable binders are susceptible to decomposition when heated to such high temperatures, and this has caused difficulties in the preparation of coloured mastic asphalt, in particular when using polymer-modified pigmentable binders.

Therefore, it would be advantageous if there was a pigmentable binder which had a relatively low workability temperature as well as good rheological properties.

JPA 2001-253988 describes a colouring resin having plate-out resistant characteristics. Plate-out is a phenomena associated with extrusion moulding which results in the formation of scratches and defects in the appearance of a moulding. The colouring resin of JPA 2001-253988 contains a styrene-based resin, a pigment, a fatty acid and a metal soap. The fatty acid amide and metal soap are added as dispersing agents to disperse the pigment uniformly in the resin, a specified ratio of amide to metal soap being required to prevent plate-out and to ensure that the pigment is uniformly dispersed. The colouring resins of JPA 2001-253988 are for use in extrusion moulding and would be unsuitable as binders in synthetic asphalt.

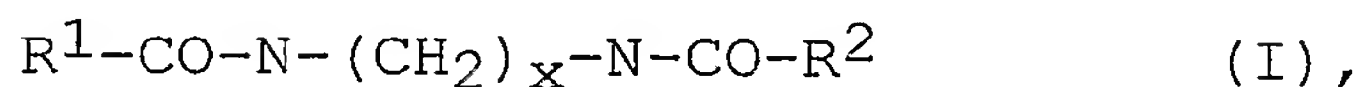
JPA 01-242667 relates to a road marking material that may be used in both hot and cold conditions. The marking materials of JPA 01-242667 contain a binder resin and a bisamide of specific melting point, the bisamide apparently being incorporated to improve the drying properties and contamination resistance of the material in hot conditions, and the cracking properties in cold conditions. JPA 01-242667 describes a road marking material: no mention is made of synthetic asphalt compositions or pigmentable binders for use therein.

Summary of the invention

It has now surprisingly been found possible to lower the workability temperature of a pigmentable binder without adversely affecting its rheological properties, by incorporating into the binder a small amount of a particular type of amide additive.

Accordingly, the present invention provides a pigmentable binder composition for use in synthetic asphalt, which composition comprises a resin, a lubricating oil and/or a lubricating oil extract, and in

the range of from 0.05 to less than 3 % wt based on total composition of an amide additive of general formula:



wherein R^1 and R^2 each independently represent alkyl groups having in the range of from 10 to 60 carbon atoms, and x is an integer in the range of from 1 to 4.

Detailed description of the invention

The pigmentable binder composition of the present invention preferably comprises in the range of from 1 to 70 % wt of a resin, more preferably 10 to 60 % wt, even more preferably 20 to 55 % wt, and most preferably 30 to 50 % wt, based on total composition.

A wide range of resins may be used in the pigmentable binder compositions of the present invention.

Resins that may be conveniently utilised include petroleum resins, e.g. petroleum resins prepared by polymerisation of unsaturated hydrocarbons present in unsaturated petroleum fractions, such as thermally cracked fractions and unsaturated hydrocarbons obtained from pyrolysis of hydrocarbons; and coumarone-indene resins e.g. resins prepared by polymerisation of unsaturated hydrocarbons present in coal tar distillates.

Coumarone-indene resins are, however, becoming less commercially attractive because they are of limited availability, are expensive, and have significant benzene content (and thus are of environmental concern).

Preferably, the pigmentable binder of the present invention comprises an acidic resin having an acid value in the range of from 0.5 to 200 mg KOH/g, more preferably 1 to 100 mg KOH/g, and most preferably 1 to 50 mg KOH/g.

Preferred acidic resins according to the present invention are modified resins based on petroleum resins, said resins having been modified so as to comprise

carboxylic acid, carboxylic acid anhydride or hydroxyl groups; resins comprising carboxylic acid or carboxylic acid anhydride groups being most preferred.

5 Such modified resins are obtainable by treating petroleum resins with unsaturated carboxylic acids or carboxylic acid anhydrides, or by mild oxidation. Alternatively, such modified resins may be obtained by modification of the resin preparation process, e.g. by copolymerisation of the unsaturated hydrocarbons in the
10 presence of unsaturated carboxylic acids or anhydrides, or in the presence of hydroxyl group-containing unsaturated carboxylic acids or esters thereof, such as hydroxyethyl-methacrylate.

Most preferably the resin is a modified petroleum
15 resin obtainable by treating a petroleum resin with maleic anhydride.

Neutral resins, such as NL 140 obtainable from Nevcin Polymers B.V. and Hikotack P140 obtainable from Kolon Chemicals Co. Ltd., may also be used, for example in
20 combination with an acidic resin in order to adjust the acid value of the resin component.

The pigmentable binder composition of the present invention preferably comprises in the range of from 20 to 97 % wt of a lubricating oil and/or a lubricating oil
25 extract, more preferably 30 to 90 % wt, even more preferably 40 to 80 % wt, and most preferably 50 to 70 % wt, based on total composition.

A wide range of lubricating oils and/or lubricating oil extracts may be included in the pigmentable binder
30 compositions of the present invention.

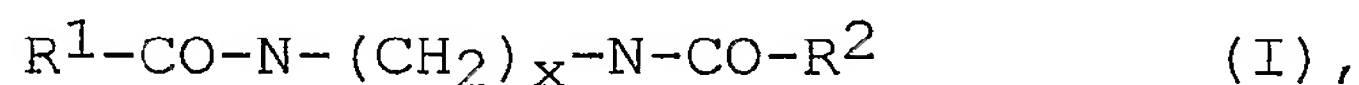
Lubricating oils which may be conveniently employed include those obtained by the distillation of crude oil or oils obtained from plants, seeds etc, e.g. vegetable oils.

Preferably, the lubricating oil and/or lubricating oil extract is a lubricating oil extract obtained by solvent extraction of a lubricating oil, most preferably by solvent extraction of a deasphalted oil (i.e. a lubricating oil obtained by the removal of asphaltenes from a residue of crude oil distillation). Lubricating oil extracts obtained by solvent extraction of a deasphalted oil are known in the art as Bright-Stock extracts, and may be obtained for example by solvent extraction of the deasphalted oil with phenol, N-methylpyrrolidone, liquid sulphur dioxide, either alone or in combination with an aromatic compound, such as benzene, or furfural.

Most preferably the lubricating oil and/or lubricating oil extract is a Bright-Stock furfural extract.

Of course, known resin-lubricating oil combinations may be utilised in the composition of the present invention. A very suitable product is sold by the Royal Dutch/Shell Group of companies under the trade name "Mexphalte C".

The pigmentable binder composition of the present invention preferably comprises in the range of 0.1 to less than 3 % wt of an amide additive of general formula



wherein R^1 and R^2 each independently represent alkyl groups having in the range of from 10 to 60 carbon atoms, and x is an integer in the range of from 1 to 4; more preferably in the range of from 0.1 to 2.5 % wt, even more preferably 0.1 to 2.0 % wt, and most preferably 0.1 to 1.5 % wt, based on total composition.

Preferably, R^1 and R^2 each independently represent alkyl groups having in the range of from 12 to 30 carbon

atoms, more preferably 14 to 20 carbon atoms. Preferably, x is an integer in the range of from 2 to 4. Most preferably x is 2 (i.e. $(\text{CH}_2)_x$ most preferably represents an ethylene group).

5 An amide additive that has been found to give particularly good results when employed in the pigmentable binders of the present invention is ethylene bis-steramaide, i.e. wherein in general formula (I) X is 2 and R^1 and R^2 each independently represent alkyl groups having
10 17 carbon atoms. Accordingly, it is preferred that the amide additive of general formula (I) is an ethylene bis-steramaide.

 Amide additives of general formula (I) may be prepared by known chemistry, or obtained from commercial
15 suppliers. An example of a preferred amide additive of general formula (I) is obtainable from Henkel KGaA under the designation "Loxamid EBS" or from Croda under the designation "Crodamid EBS".

 In a preferred embodiment of the present invention
20 the pigmentable binder composition further comprises a polymer. The present invention is of particular benefit when applied to such polymer-modified pigmentable binder compositions as the polymeric components of the composition are particularly susceptible to decomposition
25 at high temperature.

 Polymers that may be conveniently employed in the compositions of the present invention include natural or synthetic rubbers, e.g. optionally hydrogenated, linear or branched (e.g. radial) block copolymers of styrene and a
30 conjugated diene (e.g. butadiene or isoprene); and thermoplastic polymers (plastomers) such as polypropylene, ethylene vinyl-acetate copolymers, polyvinyl chloride and polystyrene.

Preferred polymers for use in the present invention are thermoplastic rubbers, most preferably block copolymers comprising at least two terminal poly(monovinyl aromatic hydrocarbon) blocks and at least one central
5 poly(conjugated diene) block, forming a continuous network, e.g. styrene-butadiene-styrene (SBS) or styrene-isoprene-styrene (SIS) block copolymers.

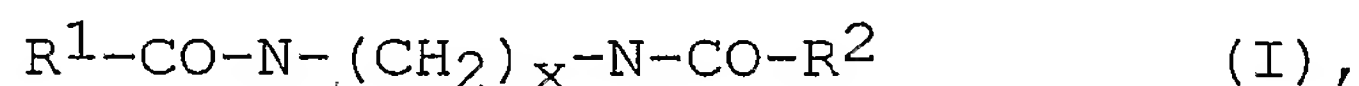
The pigmentable binder composition of the present invention preferably comprises in the range of from 1 to
10 15 % wt of a polymer, more preferably 3 to 12% wt, and most preferably 5 to 10 % wt, based on total composition.

The compositions of the present invention may comprise a single type of polymer or a combination of two or more types of polymer. In a further preferred
15 embodiment of the present invention, the compositions comprise a thermoplastic rubber and a plastomer, more preferably a styrene-butadiene-styrene block copolymer and an ethylene vinyl-acetate block copolymer or an atactic polypropylene. When the compositions of the
20 present invention comprise both a thermoplastic rubber and a plastomer the amount of thermoplastic rubber is preferably in the range of from 3 to 10 % wt; and the amount of plastomer is preferably in the range of from 2 to 5 % wt, based on total composition.

25 The pigmentable binder of the present invention may further comprise minor proportions of other ingredients commonly used in pigmentable binder compositions such as tackifiers, e.g. lithium salts of C₁₀₋₄₀ (hydroxy) fatty acids. Preferably, the pigmentable binder compositions do
30 not contain any substantial amount (i.e. greater than 1 % wt) of bitumen, and most preferably contain no bitumen.

The pigmentable binders of the present invention, may be conveniently mixed with aggregate to form synthetic asphalt compositions. Accordingly, the present

invention further provides a synthetic asphalt comprising a mixture of aggregate and a pigmentable binder composition which comprises a resin, a lubricating oil and/or a lubricating oil extract, and in the range of from 0.05 to less than 3 % wt based on total composition of an amide additive of general formula:



wherein R^1 and R^2 each independently represent alkyl groups having in the range of from 10 to 60 carbon atoms, and x is an integer in the range of from 1 to 4.

Preferred pigmentable binders described hereinabove with regard to the pigmentable binder of the invention are similarly preferred with regard to the synthetic asphalt of the invention.

The amount of pigmentable binder in the synthetic asphalt of the present invention may vary depending on the application for which the synthetic asphalt is to be used. For example, synthetic mastic asphalt compositions will typically contain a larger amount of binder than a continuously graded asphalt. However, the synthetic asphalt of the present invention preferably comprises in the range of from 1 to 15 % wt of pigmentable binder, based on total synthetic asphalt.

A wide range of aggregate type and size distribution may be present in the synthetic asphalt composition of the invention. Suitable aggregates include stones, sand and fillers such as mineral dust and ground limestone. Conveniently the aggregate employed in the synthetic asphalt of the present invention may be a combination of filler (particles having a particle size of less than 63 micrometers) and larger aggregates such as sand (particle sizes of from 63 micrometers to 2 mm) and stones

(particles sizes of greater than 2 mm, preferably in the range of from 2 to 20 mm).

5 In order to impart a particular colour to the asphalt, the synthetic asphalt composition may further comprise from 0.01 to 10 % wt of a pigment, preferably 0.02 to 2 % wt, based on total synthetic asphalt composition. Pigments which may be conveniently used include red and yellow iron oxides, titanium oxide (white), chromex green, and cobalt blue.

10 Mastic asphalt is a type of asphalt that contains a large proportion of filler. The high percentage of filler gives mastic asphalt a smooth surface. Further, mastic asphalt is a largely impermeable material, the void content of mastic asphalt generally being below 1%.
15 These properties make mastic asphalt a good material for use as indoor and industrial flooring. However, the high filler content means it is generally necessary to heat a mastic asphalt mix to a very high temperature before it becomes workable for application. Accordingly the
20 present invention, which allows workability temperatures to be lowered, is particularly advantageous for use with synthetic mastic asphalt. Therefore, in a preferred aspect of the present invention the synthetic asphalt is mastic asphalt.

25 When the synthetic asphalt of the present invention is a mastic asphalt it is preferred that the amount of filler in the asphalt is at least 15% wt, based on total synthetic asphalt, more preferably at least 20% wt, even more preferably at least 25% wt and most preferably in
30 the range of from 25 to 40% wt. Further, when the synthetic asphalt of the present invention is mastic asphalt it is preferred that the amount of pigmentable binder composition is at least 5% wt, more preferably at least 6% wt and most preferably in the range of from 6 to

15 %wt, based on total synthetic asphalt composition. The present invention further provides for the use of a pigmentable binder according to the present invention in synthetic mastic asphalt.

5 The invention will be further understood from the following illustrative examples.

Examples 1-3

In Examples 1-3 the various materials/additives are designated as follows:-

- 10 i) "Mexphalte CP2" is a commercial polymer-modified pigmentable binder obtainable from member companies of the Royal Dutch/Shell Group. ("Mexphalte" is a trade mark). This binder comprises a modified
15 petroleum resin having an acid value in the range of from 10-16 mg KOH/g, a Bright-Stock furfural extract, and approximately 9 % wt of polymeric components.
 ii) "EBS" is a commercial ethylene bis-stearamide obtainable under the designation "Loxamid EBS" from "Henkel KGaA".

20 Three separate batches of "Mexphalte CP2" were each blended at a temperature of 140 to 145 °C, with a respective 1.0% wt, 1.5 % wt and 2.0 % wt of EBS, based on total binder composition, (Examples 1, 2 and 3).

25 The properties of the untreated "Mexphalte CP2" (Comparative Example A) and EBS-containing compositions are shown in Table 1 (penetration values were determined at 25 °C according to EN 1426; softening points were determined according to EN 1427; and viscosity measured at 180 °C using a Dynamic Shear Rheometer.)

30 Subsequently, synthetic mastic asphalt mixes were prepared by adding each of the pigmentable binder compositions described above to a respective batch of hot aggregate mixture. The amount of synthetic binder used in

each synthetic asphalt mix was 7.3 % wt, based on total composition, and the aggregate used comprised:

- 28.0 %wt filler
- 20.9 %wt 0-4 mm aggregate
- 5 16.9 %wt 2-6 mm aggregate
- 26.9 %wt 6-8 mm aggregate

10 In addition, coloured synthetic mastic asphalt mixes were prepared in the same manner as the above asphalt mixes but with the addition of 2.4 % wt of a green pigment or of a red pigment in place of a respective amount of filler. The green pigment used was Cr_2O_3 obtainable from Bayer under the trade name Chrome Oxide Green GN. The red pigment used was Fe_2O_3 obtainable from Bayer under the trade name Bayferrox 130.

15 The workability of each of the synthetic mastic asphalts and coloured synthetic asphalt mixes was determined as follows.

20 The synthetic mastic asphalt mixes were placed in a heated vessel fitted with a thermocouple and an electric stirrer. The electric stirrer was connected to apparatus for measuring the torque required to stir the synthetic mastic asphalt mixes, the torque being calculated by means of a computer program that converts the data recorded at the stirrer into a torque value.

25 In order to compare the workability of the different synthetic asphalt mixes, each of the mixes was stirred at a constant rate (17 rev. min^{-1}) whilst the temperature of the mix was increased and the torque required in order to maintain the constant stirring rate recorded. In this way
30 a correlation between torque and asphalt temperature was established for each of the mixes, and from this the temperature to which each of the synthetic mastic asphalt

samples needed be heated in order for them to have the same workability was determined.

The workability temperatures for each of the mixtures are shown in Table 1 wherein:-

5 a) workability temperature 1 is the temperature to which the synthetic mastic asphalt compositions needed to be heating in order to stir them at a rate of 17 rev. min⁻¹, using a torque of 50 Ncm; and

10 b) workability temperature 2 is the temperature to which the coloured synthetic mastic asphalt compositions needed to be heated in order to stir them at a rate of 17 rev.min⁻¹, using a torque of 35 Ncm.

TABLE 1

	Ex. A	Ex. 1	Ex. 2	Ex. 3
<u>Binder</u>				
"MEXPHALTE CP2" (% wt)	100	99.0	98.5	98.0
EBS (% wt)	0	1.0	1.5	2.0
Penetration (dmm)	41	43	41	46
Softening point (°C)	54	58	66	64
Viscosity at 180°C (mPas)	214	196	190	178
<u>Synthetic asphalt</u>				
Workability temp. 1 (°C)	234	214	224	214
<u>Green synthetic asphalt</u>				
Workability temp. 2 (°C)	245	226	230	218
<u>Red synthetic asphalt</u>				
Workability temp. 2 (°C)	255	243	238	233

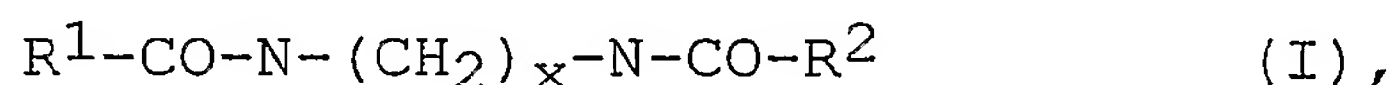
15 From Table 1 it can be seen that the pigmentable binders according to the invention (Examples 1-3) have very similar penetration values to the untreated pigmentable binder (Comparative Example A). Further, it can be seen that the synthetic mastic asphalt compositions
20 prepared from these binders have an improved workability;

the temperature to which the synthetic mastic asphalt compositions according to the invention need to be heated being in the order of 20 °C lower than those required to attain the same workability with the comparative compositions.

The above are data provided under laboratory conditions. It is believed that the compositions of the invention when used on a larger scale will enable workability temperatures of the order of less than 200 °C, and potentially less than 180 °C, to be achieved without significant change of rheological properties.

C L A I M S

1. Pigmentable binder composition for use in synthetic asphalt, which composition comprises a resin, a lubricating oil and/or a lubricating oil extract, and in the range of from 0.05 to less than 3 % wt based on total composition of an amide additive of general formula:



wherein R^1 and R^2 each independently represent alkyl groups having in the range of from 10 to 60 carbon atoms, and x is an integer in the range of from 1 to 4.

2. Pigmentable binder composition as claimed in claim 1, which further comprises a polymer.

3. Pigmentable binder composition as claimed in claim 1 or claim 2, wherein the resin is an acidic resin, having an acid value in the range of from 0.5 to 200 mg KOH/g.

4. Pigmentable binder composition as claimed in any one of claims 1 to 3 wherein the resin is a modified petroleum resin comprising carboxylic acid, carboxylic acid anhydride or hydroxyl groups.

5. Pigmentable binder composition as claimed in claim 4, wherein the resin is a modified petroleum resin obtainable by treating a petroleum resin with maleic anhydride.

6. Pigmentable binder composition as claimed in any one of claims 1 to 5, wherein the lubricating oil and/or lubricating oil extract is a Bright-Stock extract.

7. Pigmentable binder composition as claimed in any one of claims 1 to 6, wherein the amide additive of general formula (I) is an ethylene bis-stearamide.

8. Pigmentable binder composition as claimed in any one of claims 1 to 7, which comprises in the range of from 1 to 70 % wt of a resin; 20 to 97 % wt of a lubricating oil

and/or a lubricating oil extract; 0.1 to less than 3 % wt of an amide additive of general formula (I); and optionally in the range of from 1 to 15 % wt of a polymer, all weights based on total composition.

9. Synthetic asphalt comprising a mixture of aggregate and a pigmentable binder as claimed in any one of claims 1 to 8.

10. Use of a pigmentable binder composition as claimed in any one of claims 1 to 8 in synthetic mastic asphalt.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/00585

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08K5/20 C08L95/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 200212 Derwent Publications Ltd., London, GB; Class A13, AN 2002-085542 XP002205716 & JP 2001 253988 A (TOYO INK MFG CO LTD), 18 September 2001 (2001-09-18) abstract</p>	1,7
Y	<p>--- EP 0 330 281 A (SHELL INT RESEARCH) 30 August 1989 (1989-08-30) claims page 2, line 1 - line 3 --- -/--</p>	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * & * document member of the same patent family

Date of the actual completion of the international search

15 April 2003

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Name and mailing address of the ISA

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Niaounakis, M

INTERNATIONAL SEARCH REPORT

Inter^lnal Application No
PCT/EP 03/00585

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 013, no. 579 (C-668), 20 December 1989 (1989-12-20) & JP 01 242667 A (HITACHI CHEM CO LTD), 27 September 1989 (1989-09-27) abstract	1-10
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